Nanometer-scale Science and Technology
Room 2016 - Session NS+NM-WeA
Nanolithography and Patterning

Moderator: S.W. Pang, The University of Michigan

2:00pm **NS+NM-WeA1 Direct Deposition of Ordered Polymer Nanostructures in UHV via thermal Dip-Pen Nanolithography**, ***P.E. Sheehan***, *M. Yang, A.R. Laracuent,* Naval Research Laboratory*; B.A. Nelson, W.P. King,* Georgia Tech*; L.J. Whitman,* Naval Research Laboratory

In thermal Dip Pen Nanolithography (tDPN) a heated atomic force microscope cantilever controls the deposition of a solid ink, acting like a nanoscale soldering iron. tDPN has several advantages over conventional DPN. Control over writing is greatly improved deposition may be turned on or off and the deposition rate easily changed without breaking contact with the surface. In addition, imaging with a cool tip does not appear to contaminate the surface, thereby allowing in situ confirmation of the deposited pattern. Finally, tDPN can deposit a range of materials that are immobile at room temperature from semiconductors to insulators to metals. Thermal DPN is particularly suited to the deposition of polymers. To date, mylar, MEH-PPV, and poly(3-dodecylthiophene) [PDDT] have all been successfully deposited. PDDT is of particular interest as a conducting polymer with great potential for use in organic electronic devices. Using tDPN, well-ordered PDDT nanostructures have been deposited on silicon oxide and gold surfaces with layer-by-layer thickness control. By adjusting the tip heating power and the writing speed, we can vary the polymer thickness from a single monolayer (~2.6 nm) to tens of monolayers with lateral dimensions below 100 nm. Moreover, the morphology of the nanostructure suggests that the polymer strands are aligned along the path of the AFM tip. Unlike conventional DPN inks, the low vapor pressure of solvent-free polymers allows deposition in Ultra High Vacuum (UHV). We have deposited in UHV single monolayers of highly-ordered PDDT nanostructures on clean Si(001)-(2x1). The electronic and crystallographic properties of these structures will be discussed.

2:20pm **NS+NM-WeA2 Multiplexed Electroless Nanopatterning of Metallic Arrays Via Scanning Probe Lithography**, ***S.A. Backer,*** University of California, Berkeley*; M. Rolandi,* University of California, Lawrence Berkeley National Laboratory*; D. Okawa,* University of California, Berkeley*; J.M.J. Fréchet,* University of California, Lawrence Berkeley National Laboratory

Direct surface patterning of metallic species is essential for the fabrication of ever smaller nanostructures, such as electrodes, magnetic data storage devices and specific catalytic sites for localized chemical reactions. Conventional lithographic techniques based on radiation can achieve remarkable resolution and pitch. However, limitations lie in the multiplexing capabilities with the need of a separate alignment and lithography step for each metal deposited. We present a multiplexed lithographic technique based on the localized surface modification of silicon using an atomic force microscope (AFM) in fluid. The sharp tip of the AFM is used to create pinhole defects in the thin oxide present on the silicon surface. Spontaneous electroless deposition of the metal ions dissolved in the fluid occurs at the defect sites creating metallic islands as small at tens of nanometers. We demonstrate the fabrication of high pitch arrays of as many as thousands of islands of Au, Co, Sn and Fe. By consecutively exposing a sample to various metallic salts in solution, nano islands composed of different metals can be deposited in a single patterning session without needing to realign the sample or change the probe. This allows for the fabrication of multiplexed intergiditated arrays of nanostructures that could be used for orthogonal catalysis.

3:00pm **NS+NM-WeA4 High-Density Gigabit Patterning of Sub-100nm Circular Hole/Dot Arrays by Nanoimprint Lithography**, ***W. Hu,*** Stanford University, U.S.A*; R.J. Wilson, L. Xu, S.J. Han, S.X. Wang,* Stanford University

High throughput and cost-effective patterning of sub-100nm periodic features is of great interest for science and engineering. In this work we present results from patterning high-density arrays of circular holes with 100nm diameters at 300nm pitch, or with 50nm diameters at 100nm pitch, throughout an area of 1 square cm. We use 75K molecular weight polymethyl methacrylate (PMMA) resist and thermal nanoimprint lithography. Several issues are addressed which arise during patterning and characterization, such as pattern distortion control during debonding and PMMA damage induced by Au metallization for scanning electron microscopy (SEM). We further demonstrate the fabrication of dense gigabit magnetic nanodot arrays using PMMA and polymethyl glutarimide (PMGI) resist bi-layers and a lift-off process. Metal residuals with different shapes are found to be associated with variable resist processing, metallization, and lift-off conditions and are removed by an ion mill process. Additionally we show that the nanodot diameter can be tuned by using oxygen plasma ashing. Finally, the magnetic properties of nanodot arrays are shown to be readily characterized by alternating gradient magnetometry (AGM).

3:20pm **NS+NM-WeA5 Advances in Nanostructure Fabrication Technology**, *G. Willson,* ***M. Stewart,*** The University of Texas, Austin **INVITED**

The drive to manufacture cheaper and more efficient semiconductor devices has inspired remarkable improvements in imaging materials science and high resolution patterning technology for several decades. Billions of dollars have been spent in efforts to devise methods and materials that enable the printing of ever smaller transistors. Microelectronic devices in full scale production today have minimum features in the range of 70-90nm and fully functional CMOS transistors with 10nm gates have been characterized. The lithographic process that has been used to generate these "nano-structures" is becoming extremely expensive and the process window or process latitude for producing them is shrinking. The cost of the imaging process threatens the economics of the semiconductor manufacturing industry. A single efficient factory equipped to produce the next generation of devices is projected to cost as much as the gross national product of countries the size of Hungary. Imprint lithography, a lower cost, high resolution patterning technology is emerging as a potential adjunct to photolithography. Some view it as a truly disruptive patterning technology. Imprint lithography loosely defines a set of techniques that includes several forms of embossing; stamping and molding that show great promise as low cost methods for producing nanostructures. These techniques take many different forms each of which has it's own special applicability. The technique we call Step and Flash Imprint Lithography (S-FIL) is designed to allow the fabrication of high resolution, high aspect ratio images that can be aligned with precision. The process accurately replicates arbitrary shapes as small as 10nm. The process can be used to define structures with very small widths but unlike photolithography, it can be used to produce very small three dimensional structures via simultaneously controlling variations in depth. A progress report on modern patterning technologies will be presented with emphasis on imprint lithography.

4:00pm **NS+NM-WeA7 Photolithography Beyond the Diffraction Limit**, ***G.J. Leggett***, University of Sheffield, UK

A scanning near-field optical microscope (SNOM) coupled to a UV laser has been used to pattern self-assembled monolayers (SAMs) of photosensitive adsorbates. Using this approach, which we call scanning near-field photolithography (SNP), it is possible to achieve a resolution of 9 nm (nearly 15 times smaller than the conventional diffraction limit) in a SAM of alkanethiols adsorbed on gold. In conjunction with a new etchant, mercaptoethylamine in ethanol, SNP-patterned SAMs have been used as resists to fabricate gold nanostructures as small as 10 nm that have sharp edge definition. Gold nanowires, 60 nm wide, have been fabricated by selective exposure of bilayers of thiol-stabilised gold nanoparticles, followed by rinsing, in a simple two-step process. The principal criterion for achieving high resolution using SNP is the excitation of a specific photochemical reaction in a group distributed with monolayer coverage on a solid surface. This encompasses a broad range of materials. This is illustrated using monolayers of chloromethylphenyl siloxanes adsorbed on silicon dioxide, which may be selectively converted to aldehydes or to carboxylate functionalities to which biological molecules may be attached. DNA nanoarrays have been fabricated that consist of 70 nm DNA spots at 500 nm spacings. These have a density 40 000 times greater than existing DNA chips, while remaining readable by far-field optical methods. Finally we demonstrate the feasibility of carrying out nanophotolithography on aluminium surfaces. Monolayers of aryl azide terminated phosphonic acid adsorbates, which exhibit substantially enhanced ambient stability compared to alkanethiol SAMs, have been formed and selectively functionalised using SNP, in a process 50 - 100 times faster than the alkanethiol patterning process. These illustrations indicate that SNP is a powerful, flexible and straightforward technique for the execution of specific surface chemical transformations.

4:20pm **NS+NM-WeA8 SPM Nanolithography of ZrN Thin Films: Nitrogen-Enhanced Growth and Hollow Oxide Feature Formation**, ***N. Farkas***, *E.A. Evans, R.D. Ramsier,* The University of Akron; *J.A. Dagata,* National Institute of Standards and Technology

A systematic study of the scanning probe microscope (SPM) oxidation of sputter-deposited ZrN thin films is presented. Based on data covering an extensive range of parameters such as exposure time, voltage, humidity and nitrogen content of the sputtering plasma, we propose a four-stage oxidation kinetics model for ZrN. We find that the heights of the oxide features are significantly larger when the films are prepared with substantial nitrogen content in the deposition plasma, whereas small nitrogen flow rates yield oxidation rates similar to Zr films. In the intrinsic part of the SPM oxidation, the oxide density increases until the volume of the oxide is about twice that of the consumed ZrN. Further oxide growth is sustainable, and in fact faster yet controlled, as the system crosses over from the space charge limited to a nitrogen-enhanced growth regime. Most striking and different from other material systems is that high-voltage SPM oxidation of ZrN generates micrometer high features that are an order of magnitude higher than the thickness of the films. Selective etching of the oxides and nitrides reveals that as the oxidation reaches the ZrN/silicon interface delamination occurs resulting in hollow oxide feature formation through stress-induced plastic flow. Interpretations of the underlying processes and film properties responsible for the unique behavior of ZrN in all regimes are provided along with an explanation for the observed non-linear voltage dependence.

4:40pm **NS+NM-WeA9 High Resolution Electron Beam Induced Etching of Extreme Ultraviolet (EUV) Lithography Mask Films**, ***M.G. Lassiter***, *P.D. Rack,* University of Tennessee; *T. Liang,* Intel Corp.

The application of EUV wavelengths for lithography is emerging as a viable technology to extend the production of small feature sizes for integrated circuits and nanotechnology. In order to make EUV lithography commercially viable, production of the mask requires the repair of defects found during the mask inspection. Traditionally, the highest resolution mask repair technology involves using a focused ion beam (FIB) of Gallium ions to physically sputter away material for etching and to induce dissociation of a precursor gas to deposit material for repairs. Some of the Gallium ions are implanted into the surface of the mask and leave undesirable effects such as reduced transmission of clear area repairs in photomasks and reduced reflection of the clear area of EUV masks. The use of electron beam induced processes for the repair of EUV masks has recently been developed as an alternative to FIB repair of masks. The electron beam induces the dissociation of a precursor gas to cause a reaction at the surface of the mask. This reaction either deposits material or causes the etching of the mask material, depending upon the type of precursor used and the substrate material. This work focuses on the latter case of electron beam induced etching (EBIE). Electron beam provides superior spatial resolution than that of the FIB, so the EBIE process can be more effective in small mask feature repairs. Also, the electron beam will not damage the mask materials because of the relatively small mass of the electron and relatively low energy used in the electron beam. This work characterizes the process of high resolution EBIE of Tantalum Nitride based EUV mask films. The effects of electron beam parameters such as accelerating voltage, beam current, and the scanning parameters are investigated. Furthermore, the use of various precursor gases is examined, and the effects on spatial resolution, etching rate, and selectivity against other materials are determined.

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